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(57) Abstract

An aqueous polymerizable composition comprising: (1) a water-soluble, water-miscible, water-dispersible or water-emulsifiable monomer such as - (a) acrylamide or the N-methylol derivative thereof or (b) multi-functional monomers such as polyacrylates of polyols and polyglycols and (2) a primary component such as a dyestuff or pigment, a filler or a plasticiser. The compositions are curable by radiation or otherwise and are useful as ink or other coating compositions, binding compositions or foaming compositions.

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AQEOUS POLYMERIZABLE COMPOSITIONS

The present invention relates to water-based compositions, and methods of operation using the water-based compositions. Whilst initially developed in relation to inks and related printing methods, the composition and method of the invention have been found to be equally efficacious in other coating, and in binding, environments.

Most current coatings and binders consist of compositions which form a film or lattice as the carrier therefor evaporates. These compositions generally comprise inert dispersed solids or soluble substances of desired properties, which properties are obtained on evaporation. In printing applications in particular, these properties (viz. film hardness, gloss, adhesion) must be achieved rapidly in order for the substrate to withstand high substrate velocity through the press. Thus enormous quantities of energy are required to be expended and "fast" organic solvents are used, thereby introducing fire hazard and pollution problems.

The use of water-based inks as a substitute for solvent-based products is not novel per se. Hitherto, such water-based inks were in the form of dispersion polymers. However, while water-based inks had potential advantages over solvent-based inks - such as cost savings, elimination of fire hazard, reduction in air pollution and more importantly the absence of a hydrocarbon base (hydrocarbons being subject to increasing shortages and subsequent price rises) - they also had numerous disadvantages such as difficulties with pigment dispersion, gloss, film thickness, curing time and flow characteristics which difficulties resulted in aqueous inks

based on dispersion polymers not being attractive.

Against this background, the principal object of the invention is seen as the provision of a water-based ink which obviates the disadvantages inherent in prior art aqueous inks as indicated above (without resurrecting the disadvantages associated with solvent-based inks) and which, at the same time, is inexpensive, easy to apply, and devoid of toxicity. Further objects include the provision of other water-based coating and binding compositions which (as our research developed) were found to be (i) superior to such compositions of the prior art, and (ii) within the ambit of our inventive concept. These will be elaborated hereafter.

Accordingly, in one broad aspect, the invention provides a polymerizable water-based composition comprising a primary component and an aqueous monomer system, wherein the said system comprises at least one water-soluble or water-miscible (or -dispersible or -emulsifiable) monomer; the composition being curable by radiation or otherwise.

In the foregoing system, a reactive monomer or monomer mixture is used which is soluble (or emulsifiable etc. as indicated above) in a very economical carrier viz. water. The water carrier imparts a fluidic mobility to the composition. It is not necessary for this carrier to be removed by evaporation for the composition to attain its desired physical properties. The composition may be cured to a solid polymer, with carrier (or proportion thereof) in situ, by the application of radiation. The radiation may be of any type (e.g. heat, U.V., I.R., electron beam, gamma and other radiations) which is able to initiate and sustain polymerization.

The expression primary component is defined by reference to the aspects of the invention in which the composition, and related methods, are applied. In its coating aspect, where the composition is applied to a suitable substrate, the component may include pigments, or dyestuffs or like coating compounds, supplemented (or partially or wholly replaced as appropriate) by non-reactive water borne components. In other aspects of the invention, it may be an appropriate filler (the invention having application as a binder for various solids - and also as a foamable preparation). The nature and use of the composition for each such purpose, along with other contemplated component ingredients, are elaborated in the ensuing description of preferred features of the invention.

In its method aspects, the present invention firstly provides a method of coating on a suitable substrate. Broadly this method comprises the steps of applying the above-defined polymerizable water-based composition to a said substrate; and subjecting the so applied composition to curing (e.g. by exposure to heat, U.V., I.R., electron beam, gamma or other radiation), whereby the aqueous monomer system reacts to form a hydrophobic polymer (the water present being rapidly lost e.g. by being absorbed into the substrate and/or by evaporation). In a further aspect the invention provides a method of binding or foaming. In this aspect, the method comprises the steps of mixing the aforesaid aqueous monomer system with the appropriate primary component, and catalyst as and if required, and subjecting the resultant

system/component to curing as above defined.

By controlling the rate and ultimate extent of water release, the resultant coating flexibility can be controlled. Further methods aspects of the invention will be set forth hereafter.

The invention will now be described with reference to the foreshadowed preferred forms thereof. It will be understood that such details are merely illustrative of the invention, and hence are not to be limitatively construed.

In its coating aspects, the low viscosity composition, in addition to the aqueous monomer system and the appropriate coating (e.g. pigment, dyestuff et al) component - will invariably contain a said catalyst to promote curing, and may also contain one or more of the said non-reactive water borne components (such as emulsions, dispersed or dissolved resins, polymers, and the like). The composition will generally be formulated in the light of such factors as the type of coating required and the type of radiation to be employed. For example, when curing is carried out by means of electron beam radiation, a catalyst is not required.

In its binding and foaming aspects, the aqueous monomer system is invariably associated, as required, with filler(s), plasticizer(s), catalyst(s) and foaming agent(s). The filler may be selected from those set forth hereafter. This aspect features a dispersion of solid in mobile fluid, the composition being curable as by radiation or by the use of (e.g.) free radical-producing catalysts.

The especially preferred aqueous monomer system is a

one-part monomer system; however, a two- or three-part monomer system may also be used. These are described in further detail below.

The aqueous (water-soluble ... -emulsifiable) monomer may be selected from any such monomer and mixture thereof. Examples of such monomers include acrylic and methacrylic acid and derivatives thereof; acrylamide and N-methylol acrylamide and derivatives thereof; modified acrylamide, especially acrylamide modified with aldehydes and the like to ultimately form polymerization-condensation type polymers; and pyrrolidones such as vinyl pyrrolidones and mixtures thereof.

Referring in particular to water-emulsifiable monomers, such monomers are typified by multi-functional monomers which, in turn, are specifically exemplified by Pentaerythritol Triacrylate (PETA), Trimethylolpropane Triacrylate (TMPTA), 1,6 Hexanediol Diacrylate (HDODA), Tetraethylene Glycol Diacrylate (TEGDA), Trimethylolpropane Trimethacrylate (TMPTMA)

The catalysts (mentioned above) are generally conventional free radical-producing components which are chosen in accordance with the type of radiation (heat, U.V., et al), or other curing, to be employed. Their purpose is to initiate and/or increase the rate of reaction. The catalysts may be (e.g.) U.V. photoinitiators or free radical-producing catalysts (either alone or as redox couple) or other type - and, as specific examples, there are mentioned persulphates (e.g.

ammonium persulphate), peroxides, AZDN, together with various reducing agents such as sodium bisulphite, sodium formaldehyde sulphoxylate, and zinc formaldehyde sulphoxylate. The benzildimethylketal compound known as "IRGACURE 651" (a Registered Trade Mark of Ciba-Geigy) is a typically suitable compound for promoting (the initiating effect of) U.V. radiation. Where curing is effected by electron beam radiation a catalyst is not required. The catalyst may be added simultaneously with the monomer. Alternatively, it

may be added subsequently together with other optional conventional additives (such as fillers), or as prior application to the substrate upon which the composition is subsequently to be applied.

The plasticizer, which functions to improve the flexibility of the cured composition, is preferably a humectant plasticizer. Typical examples are calcium and zinc chloride, sugar, glycerine and glycols; other examples include synthetics such as starch and starch derivatives, polyvinyl alcohol, gum and modified cellulose. The aforesaid non-reactive water borne components, which are exemplified by emulsions or dispersed or dissolved resins or polymers, do not take part in the polymerization reaction. However, they are easily dispersed or dissolved in the compositions and function to improve the end properties.

In the printing ink applications, where the coating weight is very low, oxygen inhibition can be a performance problem. In one optional form of the invention, we overcome the problem by externally applying nitrogen to the printed substrate. Alternatively we may add to the system chemicals which form in situ carbon dioxide or nitrogen during polymerization, such chemicals being for example latent CO_2 producing alkali (e.g. basic carbonate for an acidic formulation). In two-part monomeric systems, acid-base reactants may be used, such as hydrochloric acid and basic carbonate (e.g. sodium bicarbonate or ammonium carbonate). In the one-part monomeric system, a basic carbonate alone may be used. The monomer system during reaction turns acid and

thus subsequently reacts with the carbonate alkali to ultimately form CO_2.

Amplifying in respect of the monomeric systems, a three-part system may comprise a first water-soluble or -miscible (or-dispersible) monomer part, a second part including plasticizer (e.g. a low-cost carbohydrate plasticizer), an acid and a free-radical catalyst, and a third part comprising a plasticizer, a CO_2 inclusive alkali and a reducing redox couple. The three parts may be mixed and, when so mixed, foaming and polymerization take place.

A two-part monomer system may have one part including a water-soluble or -miscible (or -dispersible) monomer, a plasticizer (e.g. a carbohydrate plasticizer), a CO_2 inclusive alkali and a U.V. catalyst, and a second part consisting of carbohydrate plasticizer solution, and acid (the parts may be alternatively constituted as indicated in the detailed examples below). When such parts are mixed and cured (e.g. by exposure to U.V. light), polymerization, with formation of CO_2 gas, takes place. The gas so formed produces foaming and oxygen is sparged.

With two- and three-part systems, foaming commences immediately the components are combined, whereas the polymerization reaction takes longer - and thus the formed CO_2 bubbles are prematurely released. These systems are therefore not as suitable for printing (or other) thin film applications as a one-part monomer system - which is especially preferred. Such a system may comprise a water-soluble or -miscible (or -dispersible) monomer, a latent

CO_2 producing alkali, a humectant plasticizer and a U.V. catalyst. Upon exposure to a U.V. light source, polymerization commences, wherein an acidic environment is produced which in turn reacts with the alkali to form CO_2. Prior to gassing commencing, polymerization occurs and formed gas is entrapped in a viscous polymer mucilage.

As indicated above, the coating component may be a dyestuff or pigment. These terms encompass water-soluble dyestuffs, aqueous pigment dispersions, and such materials as clays (e.g. china clay) and whiting. Other additivies - such as surfactant(s) (to aid dispersion), plasticizers (as indicated above) and viscosity controllers - may also be present as required.

Of those specifically mentioned heretofore, the especially preferred water-soluble or -dispersible monomers are acrylamide or N-methylol derivatives thereof. The conventional method for producing acrylamide is by hydrating acrylonitrile in the presence of sulphuric acid and water at 100°C, thus forming acrylamide sulphate and subsequently removing the sulphate and recovering pure acrylamide. In the present invention, the acrylamide may be produced by reacting acrylonitrile in the presence of hydrochloric acid to produce acrylamide chloride. By further addition of calcium hydroxide, calcium chloride is formed. The production of calcium chloride in this way is a convenient and inexpensive means of eliminating an otherwise unwanted by-product.

Acrylamide monomer as such (without further modification) is suitable as the water-soluble or dispersible monomer.

However, modification of the acrylamide to the N-methylol derivatives adds even greater latitude to the formulation. The reaction of acrylamide with various aldehydes will form the corresponding methylol products and then upon polymerization the condensation reaction occurs simultaneously. Formaldehyde (in the form of paraformaldehyde) is the particularly preferred reactant. The percentage solids is not critical.

Turning to the other (non-ink) water-based compositions foreshadowed heretofore, the prior art problems have again been overcome. Thus, in the field of paper and board sizing, the principal problem encountered with the use of prior art acrylic emulsions was in the difficulty in removing the residual carrier, which resulted in the use of considerable energy during the drying operation. This problem is obviated by the present invention. Where the compositions of the invention are used as alternative coating compositions, such compositions may be applied to a substrate using conventional techniques and cured using such methods as described above. Typical substrates include paper, board, wood, metal masonry, glass, cloth synthetic surfaces, woven and non-woven textile fabrics (including polyester and other natural and synthetic fibres for use in such fabrics) and the like.

In binding applications of the invention, the compositions may contain conventional solid carriers (fillers) as primary component. As solid carriers there may be mentioned (ground) natural minerals, such as clays, talc, chalk, kaolins, quartz, diatomaceous earth and the like and (ground) synthetic minerals such as alumina and silicates and the like. There may also be mentioned (crushed and fractionated) natural rocks

such as marble, calcite pumice and the like as well as (granules of) organic materials such as solid synthetic polymers (e.g. polyethylene), polyester and other synthetic and natural fibres, sawdust and vegetable fibres and organic pulp such as paper pulp and the like.

The water-soluble or -miscible (or -dispersible) or emulsifiable monomer acts as a binder for such solid carriers. In one such embodiment of the present invention, methylol acrylamide together with a heat induced free radical catalyst acts as a binder for sand and/or marble chips. When moulded into a desired shape and cured by means of heat, e.g. hot platen press, heated rollers, oven dielectric, and the like, such composition cures through a polymerization condensation type reaction to form hard, dimensionally stable imitation brick. Sawdust and/or paper may be substituted for the sand and marble and marble chips and the resulting composition cured by means as described above.

In the above-mentioned cases, the advantage of the process lies in the considerable energy savings resulting from the polymerization reaction which is exothermic.

The above-mentioned carrier(s) can, of course, be augmented. Thus, plasticizer(s), stabilizer(s), dyestuff(s) and the like may also be added.

In the foaming applications of the invention, the composition may be based on the above described monomer, plasticizer(s) and foaming agent(s). The water-soluble monomer may be in the form of a two-part monomeric system, the parts (including monomer, plasticizer, catalyst et al) being as constituted heretofore or as specifically exemplified in the subsequent

examples. Alternatively, a three-part system may comprise a first monomer part, a second part incorporating a plasticizer, an acid and a free radical catalyst, and a third part incorporating plasticizer, CO_2 inclusive alkali and reducing redox couple. The components may be formulated to equal volume and mixed - with resultant simultaneous foaming and polymerization. The foam composition thus produced (where air may act as a filler material) has use, inter alia, in insulation environments and as a protective coating for animals.

The invention will now be described, in greater detail, with reference to specific working examples. The examples illustrate all aspects of the invention. Unless specifically indicated to the contrary, parts are by weight. Where implementation of the examples has involved the use of conventional proprietary compositions - which, in the art, are obtainable under, and normally identified by, trade or like names - these compositions have been so identified and in conjunction therewith, have been identified (as far as possible) by reference to their general chemical constitution. Similarly, where known commercial equipment is used (e.g. as the source of radiation in the specific examples), such equipment is identified in the manner in which it is known in the art.

Example 1

This example illustrates a three-part monomer system. The first part comprises 100 parts by weight of N-methylol acrylamide (60%) (hereinafter sometimes referred to, for convenience, simply as N.M.A.). The second part was formed from 50 parts by weight water, 45 parts by weight sugar, 3.5 parts by weight hydrochloric acid and 1.5 parts by weight ammonium persulphate and a third part from 50 parts by weight water, 45 parts by weight sugar, 1.5 parts by weight sodium formaldehyde sulphoxylate, and 3.5 parts by weight sodium bicarbonate. The three parts were mixed together in equal proportions.

Example 2

This example illustrates a two-part monomer system. The first part was produced by mixing 37.5 parts by weight water, 52 parts by weight calcium chloride, 2 parts by weight hydrochloric acid, 8 parts by weight acetone co-solvent, and 0.5 parts by weight of the catalyst known as "IRGACURE 651" (see heretofore). The second part was produced by 87 parts by weight 60% N.M.A., 5 parts by weight ammonium hydroxide and 8 parts by weight ammonium carbonate and the two parts mixed together.

Example 3

This example further illustrates a two-part monomer system. The first part was formed by mixing 66 parts by weight 60% N.M.A., 28 parts by weight 50% sugar/water solution 0.3 parts by weight "IRGACURE 651" and 5.7 parts by weight of sodium bicarbonate. The second part was produced by

mixing 90 parts by weight 50% sugar/water solution, 9 parts by weight acetone, 0.3 parts by weight "IRGACURE 651" and 0.7 parts by weight acetic acid. The two parts were then mixed together.

Examples 4-7

These examples illustrate several one-part monomeric systems. For convenience, the systems are presented in tabular form.

Ingredients	Example 4	Example 5	Example 6	Example 7
60% N.M.A.	50.5	70.5		77
Acrylamide	44.0		57.0	
Calcium chloride	5.0	16.0		
Irgacure 651	0.5	0.5	0.2	0.4
Acetone		3.0	5.0	5.0
$(NH_4)_2CO_3$		10.0	4.0	10.0
Paraformaldehyde			24.0	
Triethylamine			0.8	
Water			10.0	
Glycerine				5.0
Ammonia				3.0

In the following examples, the compositions and related methods of the invention are illustrated. As elsewhere, parts are by weight. Examples 8 to 13 illustrate the printing and other coating aspects of the invention, whilst Examples 14 and 15 illustrate the binding and foaming aspects.

Example 8

Gravure ink (black): cured by U.V. radiation.

Composition:

60% N-methylolacrylamide (water-soluble monomer)	52.0
Primal I-94 (alkali soluble polymer emulsion)	40.0
Continex N326 (carbon black pigment)	5.0
aqueous ammonia	1.0
Irgacure 651 (photoinitiator catalyst)	2.0

The Primal I-94 is neutralized with aqueous ammonia, and then added slowly, with stirring, to the N.M.A. solution. A transparent solution results. The pigment and photoinitiator catalyst are dispersed into this medium, using a bead mill, at a temperature less than 40°C. Printing, on a paper substrate, is effected using a rotogravure press. As indicated above, curing is by U.V. radiation (U.V. Curing Unit (H type bulb) of Fusion Systems Corp.).

Example 9

Flexographic ink (black) for reclaimed paper: cured by U.V. radiation.

Composition:

60% N-methylolacrylamide (water-soluble monomer)	50.0
P.V.P. K-30 (viscosity controller)	0.5
alkanate 3SN5 (surfactant) (anionic emulsifier)	0.05

Continex N326 (carbon black pigment)	7.45
water	40.0
Irgacure 651 (photoinitiator catalyst)	2.0

The P.V.P. K-30 (polyvinylpyrrolidone) is dissolved in the N.M.A. solution, and the surfactant and water are then added. The pigment and photoinitiator catalyst are dispersed as in Example 8. Printing upon the paper substrate is effected with a flexographic press. U.V. curing is carried out as in Example 8.

Example 10

Clear coating for printed paper: cured by U.V. radiation.

Composition:

60% N-methylolacrylamide (water-soluble monomer)	30.0
Primal HA-16 (polymer emulsion)	30.0
Irgacure 651 (photoinitiator catalyst)	1.0
acetone	5.0
water	34.0

The polymer emulsion is stirred into the N.M.A. solution and water is added. The photoinitiator catalyst is dissolved in the acetone, following which the dissolved catalyst is slowly added to the N.M.A. solution with high speed mixing. Coating is effected per medium of a roll coater with doctor blade. Radiation is carried out as in Examples 8 and 9.

Example 11

Transparent coating for clay coated paper: cured by electron beam radiation.

Composition:

60% N-methylolacrylamide (water-soluble monomer)	50.0
33% Platamid M1255 (water-soluble copolyamide resin)	48.0
Eriosin blue dye	2.0

The polyamide and N.M.A. solutions are mixed, and the dye is dissolved therein. Coating is effected as in Example 10. Electrom bean radiation is carried out using a 250kV electron accelerator.

Example 12

Clay coating for paper: cured by U.V. radiation.

Composition:

60% N-methylolacrylamide (water-soluble monomer)	48.0
Eckalite clay	50.0
Irgacure 651	2.0

The photoinitiator catalyst is dispersed in N.M.A. solution, using a bead or sand mill. Thereafter, the clay is dispersed in a similar manner. Coating is carried out as in Examples 10 and 11 (alternatively, the doctor blade can be substituted by an air knife). U.V. radiation is carried out as in Examples 8 to 10.

Example 13

Glazing upon ceramic tiles: cured by U.V. radiation.

Composition:

60% N-methylolacrylamide (water-soluble monomer)	35.0
powdered red glazing glass (pigment)	40.0
Sandoray 1000 (photoinitiator catalyst)	1.0
acetone	4.0
water	10.0

The N.M.A. solution is diluted with water, the photoinitiator catalyst is dissolved in acetone, and the former is added to the latter with vigorous mixing. Into the resultant medium, the glazing compound is dispersed (with continued vigorous mixing). Silk screen printing is effected, and the U.V. radiation is performed as above.

Example 14 (see Example 2)

Foaming mix: cured by U.V. radiation.

Composition:

Part A:	60% N-methylolacrylamide	87.0
	aqueous ammonia	5.0
	ammonium carbonate	8.0
Part B:	water	37.5
	calcium chloride	52.0
	hydrochloric acid (10M)	2.0
	acetone	8.0
	Irgacure 651	0.5

In relation to Part A, the aqueous ammonia and N.M.A. solution are mixed, and the ammonium carbonate is dissolved therein. In relation to Part B, the calcium chloride plasticizer is dissolved in water, hydrochloric acid is added, the photoinitiator catalyst is dissolved in acetone, and the solutions are mixed with rapid stirring. Foaming commences when the two parts are mixed together. Radiation may be effected by direct sunlight.

Example 15

Artificial brick: heat cured.

Composition:

60% N-methylolacrylamide	20.0
ammonium persulphate	0.1
sand filler	79.9

The ammonium persulphate catalyst is dissolved in the N.M.A. solution, following which the filler is dispersed therein. Production is carried out by continuous extrusion into an oven at 110°C for five minutes. Radiation is effected thermally (from the oven).

Example 16

Clear protective gloss coating.

Trimethylolpropane triacrylate (water-emulsifiable monomer)	25.0
Irgacure 651	2.0
Teric N9	0.5
Primal I-62 (alkali-soluble polymer emulsion)	40.0
60% N-methylolacrylamide (water-soluble monomer)	30.5
Aqueous ammonia (31%)	2.0

The irgacure 651 is dissolved in the TMPTA and Teric N9 added. This mixture is then emulsified into the clear solution resulting from the combination of Primal I-62, 60% NMA and ammonia. A high speed mixer is used to carry out the emulsification.

The coating is applied to a flexible paper substrate using a roll coater. Curing is effected by U.V. radiation as in examples 8 to 10.

Example 17

Clear protective matt coating.

Trimethylolpropane triacrylate (water-emulsifiable monomer)	30.0
Irgacure 651	2.0
Alkanate 3SN5	1.0
Teric N5	0.5
Primal ASE 60 (alkali-soluble polymer emulsion)	2.0
60% N-methylolacrylamide (water-soluble monomer)	49.0
Sucrose (plasticizer)	5.0
Water	10.0
Aqueous ammonia (31%)	0.5

The irgacure 651 is dissolved in the TMPTA and the surfactants (Alkanate 3SN5, Teric N5) are added. In another container, the remaining ingredients are combined, the ammonia being added last with stirring. The former solution is then emulsified into the latter solution using a high speed mixer.

The coating is applied by roll coater to paper. Curing is by U.V. radiation as in example 16.

In conclusion, it is reiterated that the preceding performance details, of the ink and other compositions and the printing and other methods, are not to be limitatively construed. Thus the individually specified examples (of the components and monomers) may be replaced by functional equivalents, the effect of oxygen inhibition need not be countered, the mentioned substrates can be varied as required (e.g. in examples 16 and 17 the coatings could be

applied to substrates other than paper) and so on. As long as the basic inventive criteria - predicated upon the novel application of water-soluble ... emulsifiable monomers in novel compositions and related methods - are observed, matters falling therewithin may be varied in accordance with situational requirements.

CLAIMS

1. A polymerizable water-based composition comprising a primary component and an aqueous monomer system wherein the said system comprises at least one water-soluble, water-miscible, water-dispersible or water-emulsifiable monomer, the composition being curable by radiation or otherwise.

2. A composition as claimed in claim 1 wherein the aqueous monomer system is a one-part system.

3. A composition as claimed in claim 1 or 2 wherein the monomer is selected from acrylamide or the N-methylol derivative thereof, and/or the multi-functional monomers as herein defined.

4. A composition as claimed in any one of the preceding claims wherein curing is effected, in the presence of a photoinitiator catalyst, by U.V. radiation.

5. A composition as claimed in any one of claims 1 to 3 wherein curing is effected by electron beam radiation.

6. A composition as claimed in any one of the preceding claims wherein such composition is a coating composition which is adapted to be applied to a substrate.

7. A composition as claimed in claim 6 wherein the primary component comprises a dyestuff or pigment.

8. A composition as claimed in any one of claims 1 to 5 wherein such composition is a binding composition, and the primary component comprises at least one appropriate filler.

9. A composition as claimed in any one of claims 1 to 5 wherein such composition is a foaming composition and the primary component comprises at least one plasticizer.

10. A water-based composition substantially as herein described with reference to any one of the foregoing specific examples thereof.

11. A method of coating upon a suitable substrate which comprises the steps of applying, to a said substrate, a composition as claimed in claim 6 or 7, and subjecting the so-applied composition to curing whereby the aqueous monomer system is polymerized.

12. A method as claimed in claim 11 wherein the substrate is selected from paper, board, wood, metal masonry, glass, cloth synthetic surfaces, and woven and non-woven textile fabrics.

13. A method which comprises the steps of mixing the monomer system with a said primary component, as appropriate, and subjecting the resultant mix to curing whereby the said system is polymerized.

14. A method substantially as herein described with reference to any one of the foregoing specific examples thereof.

INTERNATIONAL SEARCH REPORT

International Application No PCT/AU81/00028

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl.[3] C08F2/44, 2/48, 2/50, 2/54, C08J9/20, C09D 11/10, 3/80

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
IPC	C08F1/18, 1/20, 1/84, 2/44, 2/48, 2/50
US Cl.	260-42/53

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

AU: IPC as above; Australian Classification 09.4-33, 09.4-34, 09.4-35

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
E, X	WO, A, 81/00569, published 1981, March 5, Staybond Pty. Ltd. (& AU, A, 61909/80)	(1-14)
X	AU, A, 23410/77, published 1978, September 21, see pages 10 - 14, American Cyanamid Co.	(1-6,8-14)
X	AU, B, 22994/77(505580), published 1978, September 14, see pages 18-29, Milchem Incorporated	(1-5,8,13)
X	AU, B, 70825/74(485825), published 1976, January 8, see pages 21-32, Canadian Industries Limited	(1-7,9-14)
X	AU, B, 40421/72(479215), published 1973, October 4, see Example 24 at page 21, The Lubrizol Corporation	(1-7,10-14)
X	AU, B, 18486/70(449670), published 1972, February 10, see pages 7 and 8, The Dow Chemical Co.	(1-5,8,13)
X	AU, B, 46964/68(439432), published 1971, May 20, see pages 17-21, Dulux Australia Ltd.	(1-7,10-14)
X	AU, A, 67234/65, published 1967, June 1, Imperial Chemical Industries Limited.	(1-7,10-14)

(continued ....)

* Special categories of cited documents: [15]

"A" document defining the general state of the art

"E" earlier document but published on or after the international filing date

"L" document cited for special reason other than those referred to in the other categories

"O" document referring to an oral disclosure, use, exhibition or other means

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"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention

"X" document of particular relevance

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
14 April 1981 (14.04.81)	16-April 1981 (16-04-81)
International Searching Authority [1]	**Signature of Authorized Officer** [20]
Australian Patent Office	A.S. Moore. A S Moore

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, 16 with indication, where appropriate, of the relevant passages 17	Relevant to Claim No 18
X	GB, A, 1489365, published 1977, October 19, See Example 1, Sumitomo Chemical Company Limited.	(1-7,10-14)
X	GB, A, 1419462, published 1975, December 31, see page 6 lines 13-22 and claim 7, The Lubrizol Corporation	(1-7,10-14)
X	GB, A, 1407257, published 1975, September 24, See pages 5-10 ,Bayer Aktiengesellschaft	(1-5,9,13)
X	GB, A, 1320688, published 1973, June 20, Imperial Chemical Industries Limited.	(1-5,8,13)
X	DE, A, 2360415, published 1974, June 6, Lion Yashi Kabushiki Kaisha	(1-7,10-14)
X	CH, A, 606240, published 1978, October 31, Dynamit Nobel Aktiengesellschaft	(1-7,10-14)
X	CH, A, 562283, published 1975, May 30, Kema Nord AB	(1-5,8,13)
X	FR, A, 2202923, published 1974, May 10, Nippon Paint Co. Ltd.	(1-7,10-14)
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X	SU, A, 496287, published 1976, March 12, Laskorin B.N. (Derwent English Language Abstract)	(1-5,9,13)
X	SU, A, 476279, published 1975, November 13, Bolotov A.N. (Derwent English Language Abstract)	(1-5, 9,13)